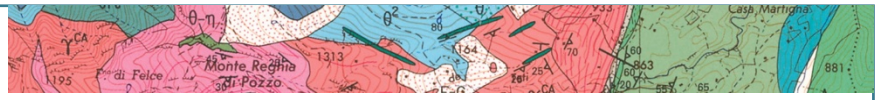


# Intrusion of $CO_2$ and oxycombustion impurities in a fresh water aquifer – impact evaluation by reactive transport modelling

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Géosciences pour une Terre durable
brgm

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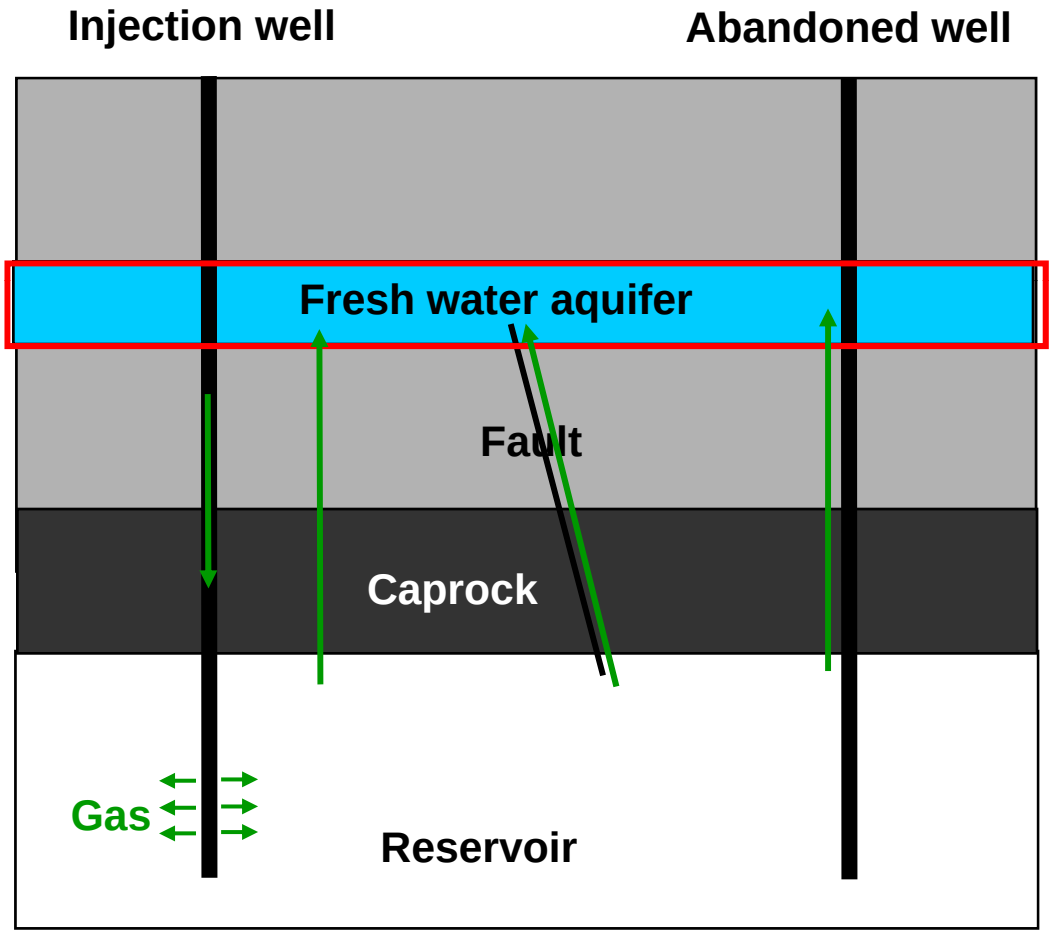
# Background

# Contamination of fresh water aquifers: an environmental risk of CCS




- **Leakage through:**
  - Caprock and overburden
  - Fault
  - Poorly abandoned well
- **Intrusion within fresh water aquifer**
- **Gas-water-rock interactions**

**--> Water quality**

# Injection of $CO_2$ + impurities

- **"Impurities" = $CO_2$ co-injected components**
- **Gas from natural gas processing in Sleipner, In-Salah CCS operations : nearly pure $CO_2$**
- **Gas from combustion process (power plants) followed by capture process : $CO_2$+impurities mixture**
  - After pre-combustion capture : reductive mixture

    $CO_2$ **>>** $H_2$, $N_2$, CO, $H_2S$ + COS, Ar
  - After oxycombustion and post-combustion capture : oxydant mixture

    $CO_2$ **>>** $N_2$ + Ar + $O_2$, $SO_x$, $NO_x$

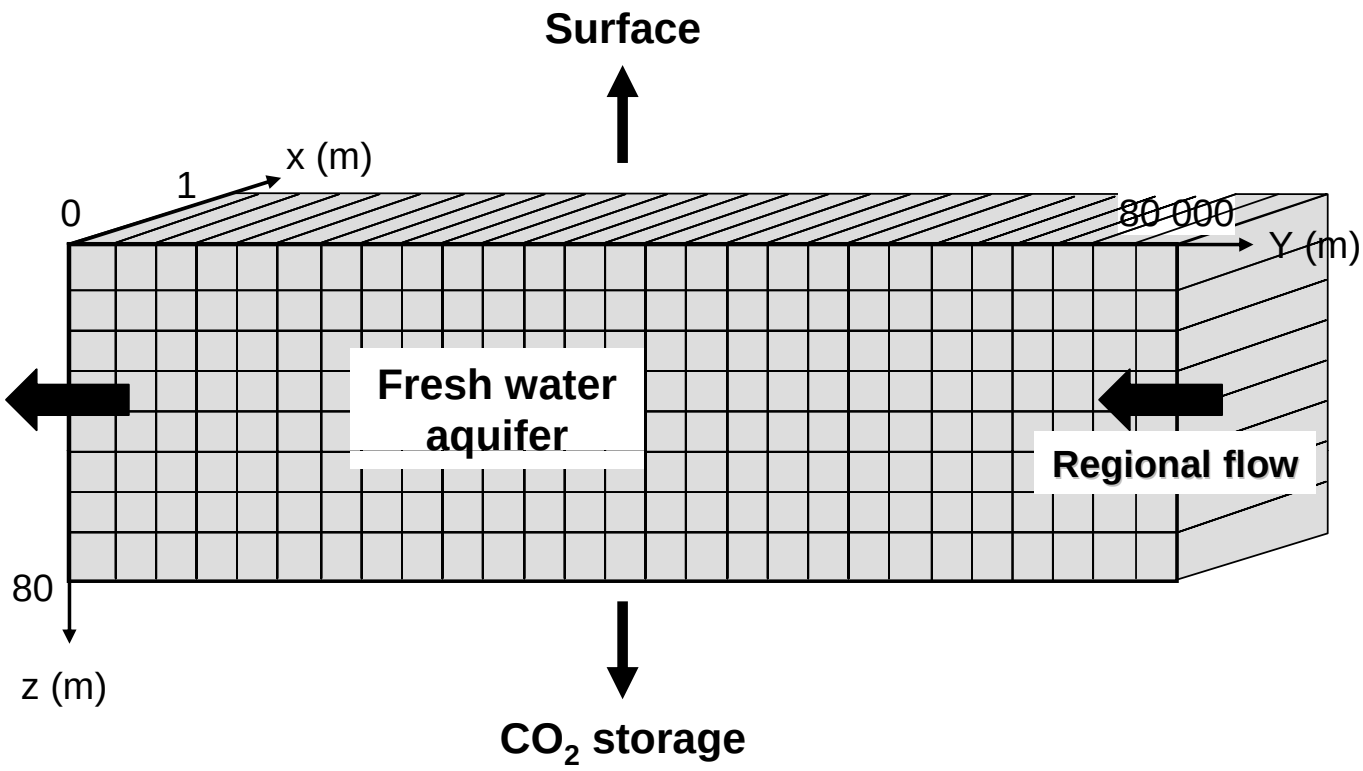
# Production of health-significant elements by gas-water-rock interactions

- **“Health-Significant Elements” (HSE) = chemical components conditioned to quality standards (limit concentrations) in potable water**
- **Two types of HSE :**
  - Carried by the contaminant gas :
    - Ex. sulphates, nitrite-nitrate and protons (pH)
  - Metals released by minerals dissolution :
    - Al, As, Ba, B, Br, Cd, Cl, Cr, Cu, F, Sn, I, Fe, Pb, Mn
- **Goal of the study :**

  **Evaluation of HSE fate in a fresh water aquifer that is subject to gas intrusion**
- **Tool : multiphase flow reactive transport simulator TOUGHREACT (Lawrence Berkeley National Laboratory)**

# Initial model set-up :
# based on the Albian aquifer,
# Paris Basin, France

# Geometry and hydrodynamics




- **2D domain, discretized into ~ 1000 cells**
- **Horizontal regional flow**
- **Homogeneous**
  - porosity, permeabilities and diffusion coefficient
  - temperature

# Chemistry: glauconitic sandstone

- **Homogeneous chemical composition within the whole domain**
- **Solid matrix = glauconitic sandstone with:**
  - primary minerals (initially present) containing HSE : Fe, Mn and Al
  - secondary minerals (not present initially but ability to precipitate) : sulphates, iron oxides
- **Interstitial water**
  - Neutral pH and reductive redox potential
- **During the runs, the mineral dissolution/precipitations are kinetically constrained**

# Model testing

# $CO_2$+impurities intrusion at 2 locations, at 2 rates

- **Intrusive fluid composition derived from an oxycombustion gas designed for injection in storage**

| | |
|---|---|
| **$CO_2$** | 90.2 % |
| **Ar** | 5.6 % |
| **$O_2$** | 1.6 % |
| **$SO_2$** | 1.5 % |
| **$N_2$** | 0.6 % |
| **NO** | 0.2 % |

Anheden *et al.* (2007)

**--> intrusive fluid has <u>maximal</u> content of $SO_2$, NO, $O_2$**

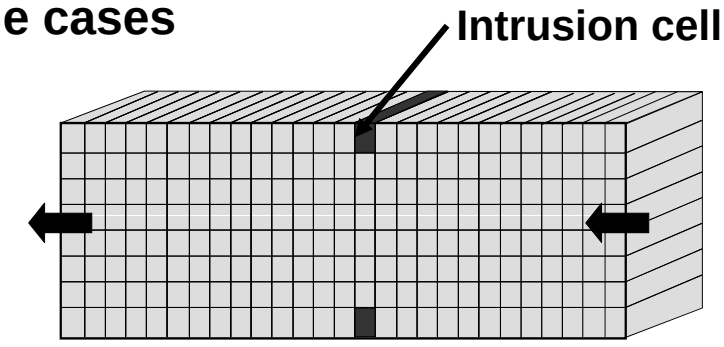
**--> worst-case scenario**

- **Low rate : (0.1 g/s) → no appearance of gas plume**

  **High rate : (1 g/s) → sufficient to make appear a gas plume**

- **Continuous intrusion during 10 y for all the cases**

- **Intrusion at top or bottom**



# Results :

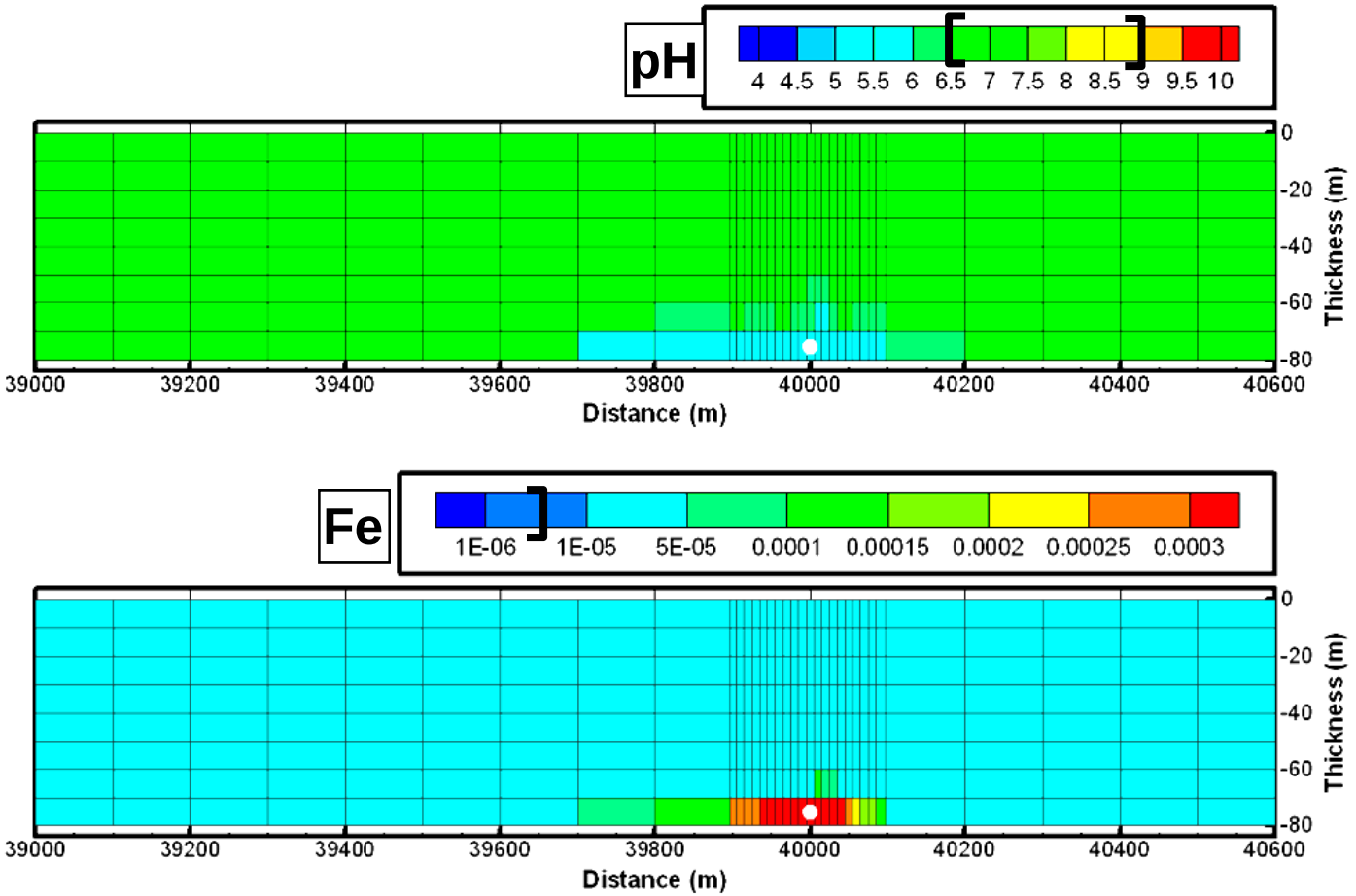
**1) Chemical reactions --> induce pollution**

**2) Physical processes --> increase pollution extent**

**3) Comparison with pure $CO_2$ intrusion --> effect of impurities**

# Acid-induced release of metals

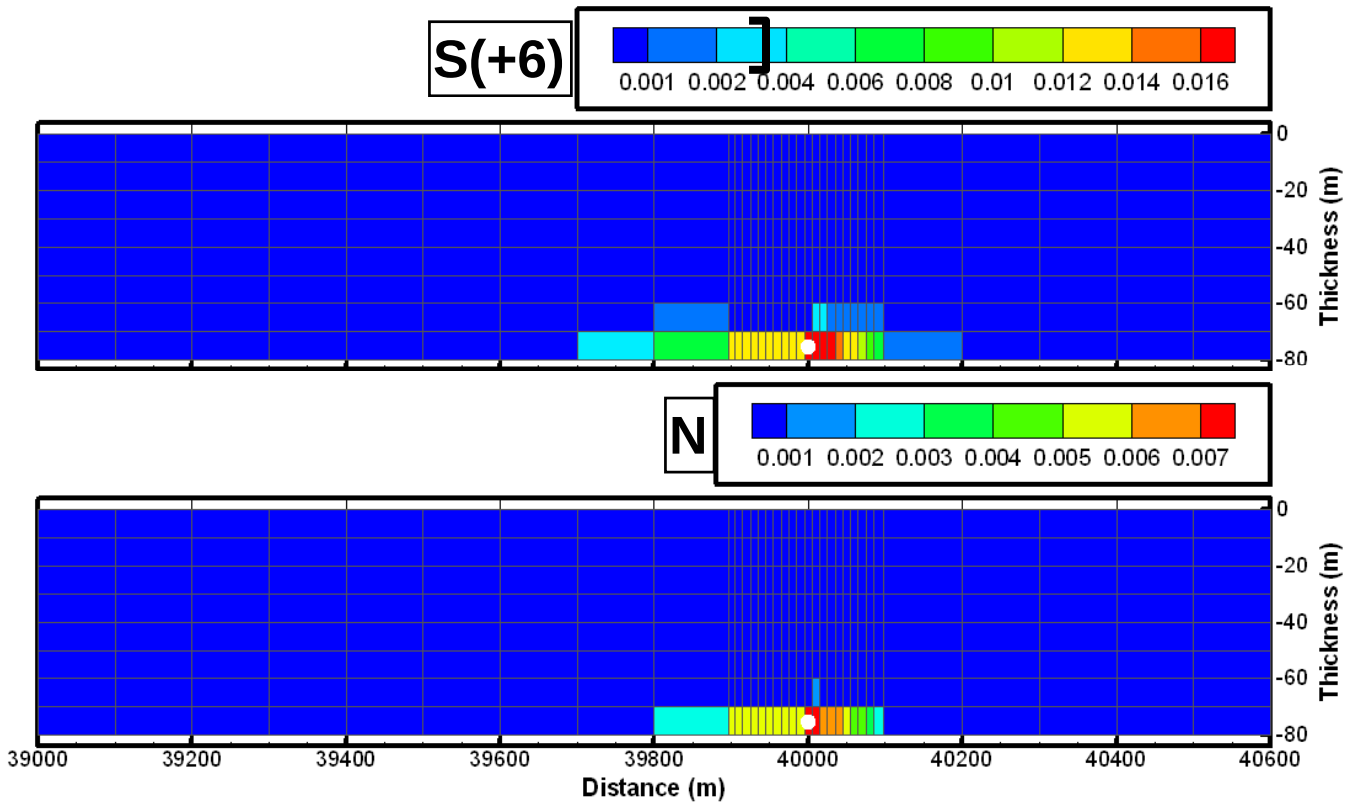
**Ex:** Low rate bottom intrusion




- Acid gases ($CO_2$, $SO_x$, $NO_x$) dissolution-reaction --> decrease of pH (acidification)
- Dissolution of Fe-carbonate and clay --> Fe release (initially slightly above limit)

# Sulphates and nitrogen from impurities

**<u>Ex:</u> Low rate bottom intrusion**




- $SO_{2(g)} + 0.5\ O_{2(g)} + H_2O \rightarrow 2\ H^+ + SO_4^{2-}$
- **We hypotesize the nitrogen to be under the form of nitrite-nitrate produced by :**

  $NO_{(g)} + 0.75\ O_{2(g)} + 0.5\ H_2O \rightarrow H^+ + NO_3^-$

## Results :

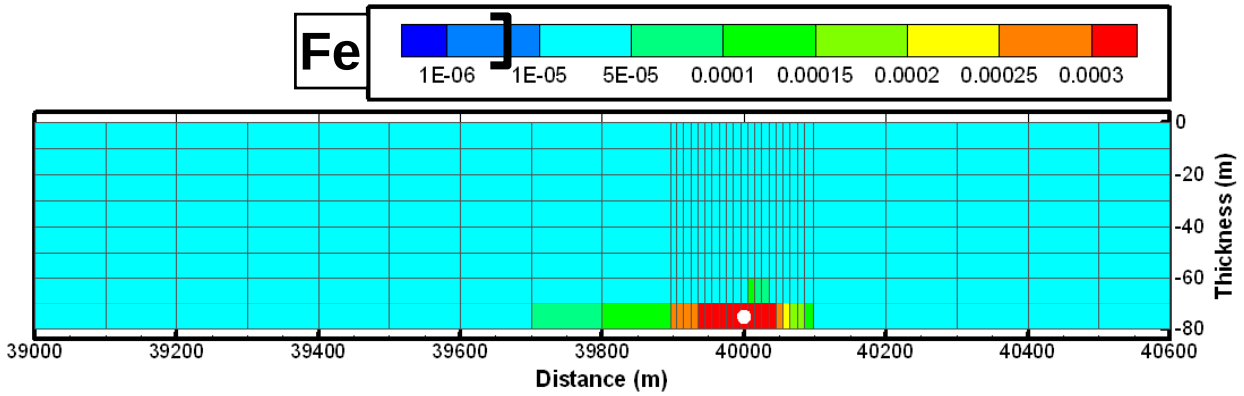
1) Chemical reactions --> induce pollution

**2) Physical processes --> increase pollution extent**

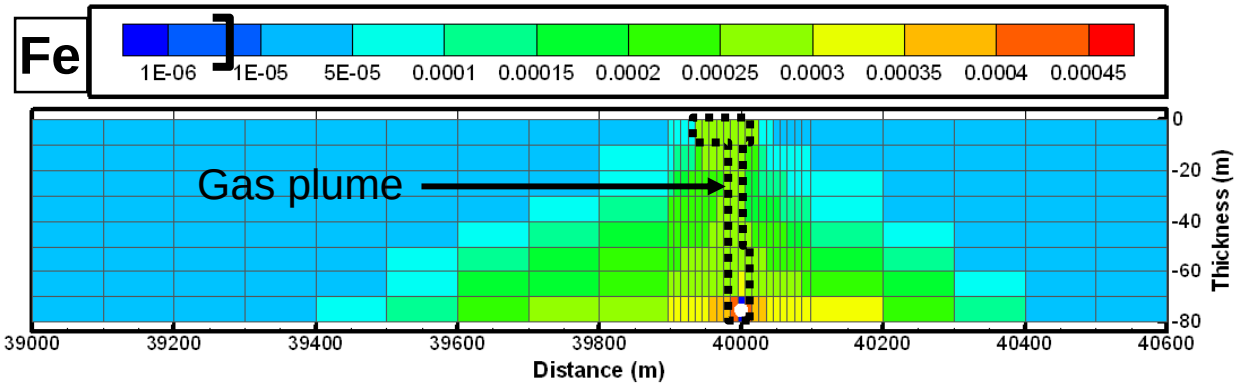
3) Comparison with pure $CO_2$ intrusion --> effect of impurities

# Influence of intrusion rate

> **HSE release and pollution lateral extent increase with the rate**




**Low rate**

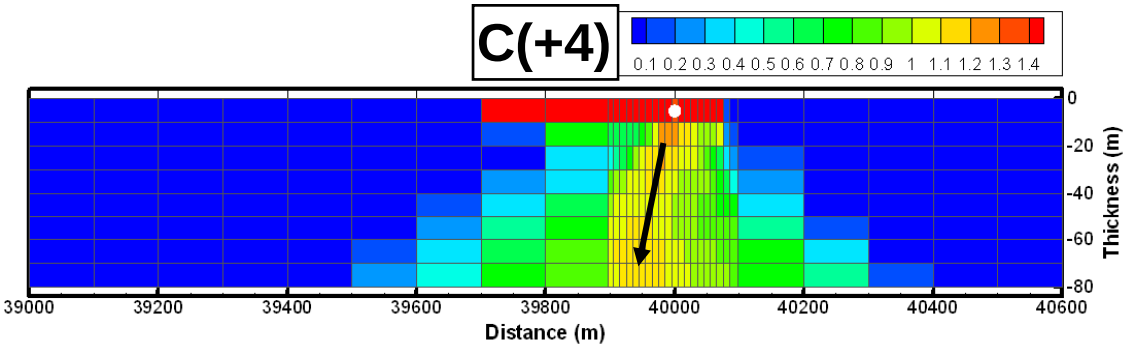



**High rate**

> **In case of bottom intrusion, if the inflow rate sufficiently high to make appear a gas plume --> migrates upward --> pollution vertical extent increase**

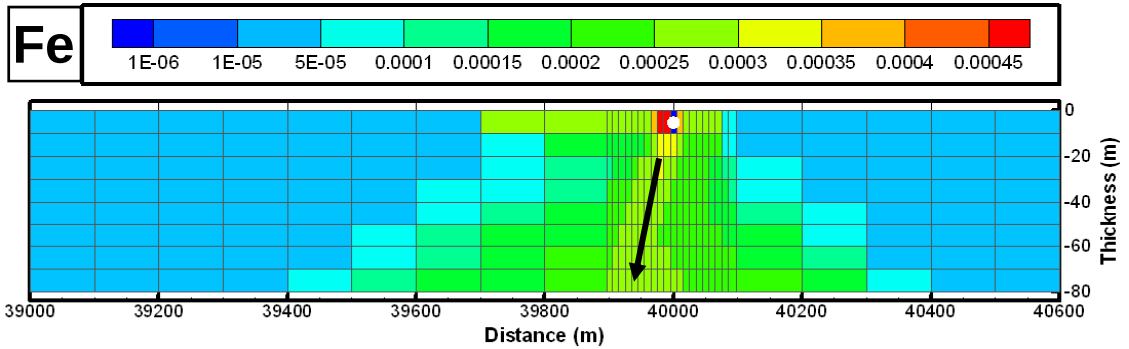
# Downward flowing of dense water

**High rate top intrusion**

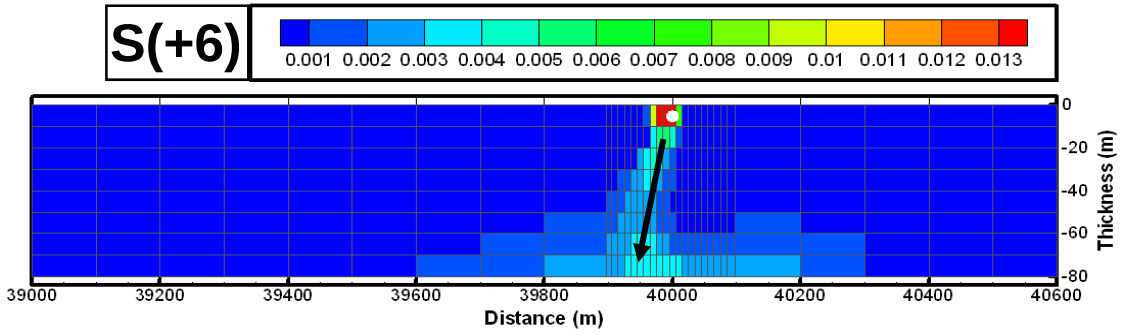



- **Strong enrichment in dissolved carbonates**

**--> makes the water denser**




- **Downward flowing carrying Fe, dissolved sulphates to the basement**



## Results :

1) Chemical reactions --> induce pollution

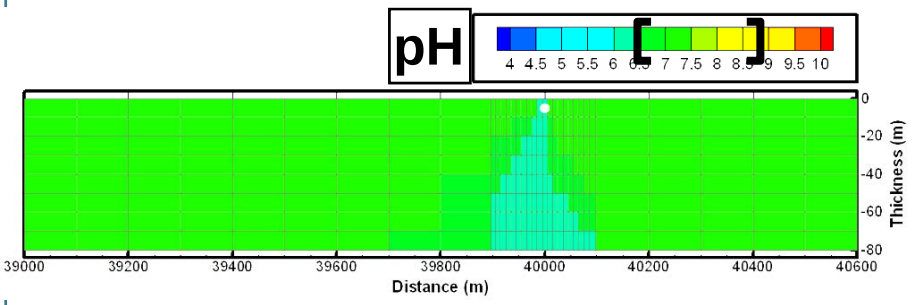
2) Physical processes --> increase pollution extent

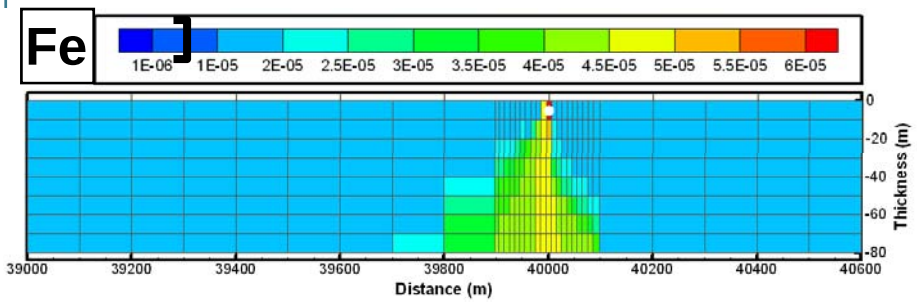
**3) Comparison with pure $CO_2$ intrusion --> effect of impurities**

# Acidification increase due to impurities presence

- Carry sulphates and nitrite-nitrate contrary to pure $CO_2$
- Presence of $SO_x$ and $NO_x$ - even in low concentrations - --> increase of acidification (very strong acid gases compared to $CO_2$)

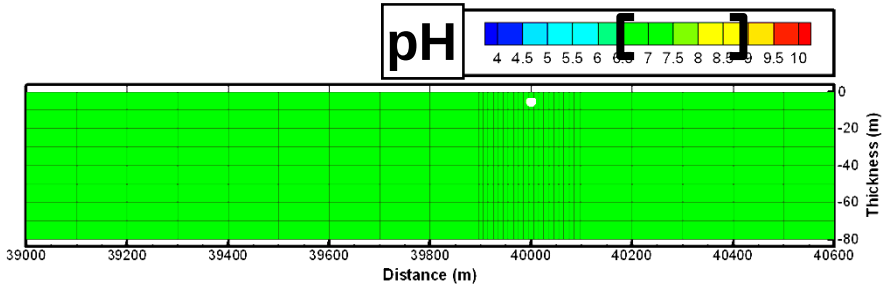
--> metal release increase

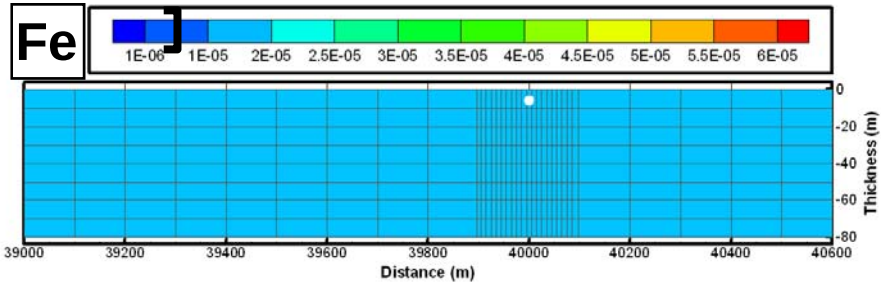



$CO_2$ + impurities

Low rate top intrusion




Pure $CO_2$

# Conclusion

- **Intrusion of $CO_2$ + $SO_x$-$NO_x$-$O_2$ within fresh water aquifer**

**--> acidification of water --> release of metals (some are HSE)**

- **$SO_x$ and $O_2$ (both from the contaminant gas) react to produce HSE sulphates**
- **Could not model realistically the fate of $NO_x$**

  **But we suspect nitrite and nitrate to be produced and to persist in the aquifer**
- **Pollution vertical extent increased by :**
  - **Upward flowing of gas plume**
  - **Downward flowing of dense carbonated water**
- **Other paper on same topic (Chan Quang Vong *et al., 2010, GHGT-10*) :**

  **- pure $CO_2$ intrusion,**

  **- heavy metals release,**

  **- natural remediation.**

# Additional slides

# Limits and perspectives

- **Choose a worst-case scenario : contaminant fluid has maximal content in $SO_x$, $NO_x$ and $O_2$ --> 'strong' contamination**

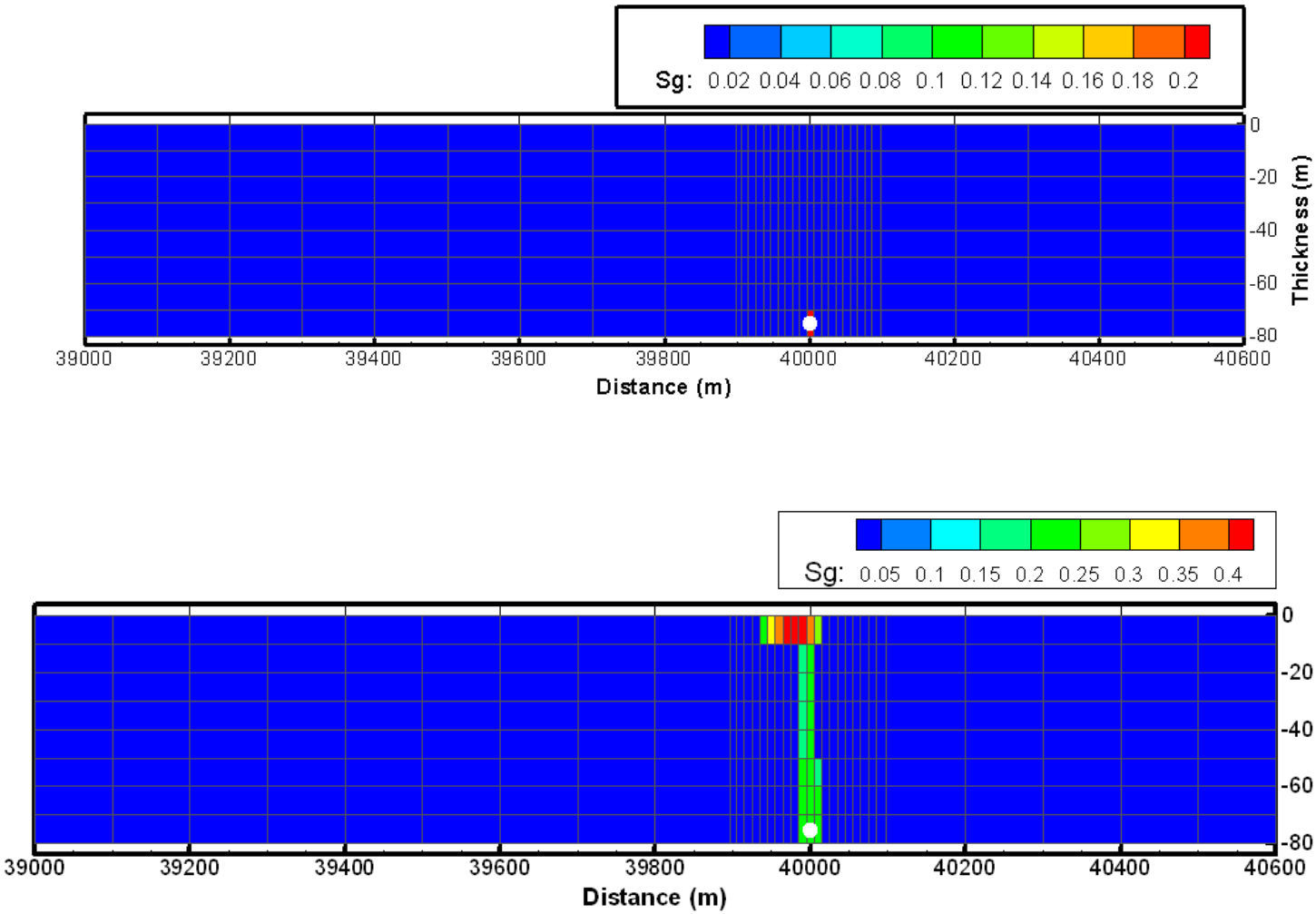
**More realistic scenario: contaminant fluid depleted in such components**

  - High solubility and reactivity of SOx, NOx --> consumption through its pathway between the reservoir and the aquifer --> minimization of the results

- **Intrusion procedure of the impurities (under dissolved species) --> transport of low-soluble impurities could not be modelled (O2, N2)**
- **Aqueous redox equilibrium assumption --> no realistic modelling of the fate of NOx**
  - Detailed study of N redox reactions (limiting steps)
- **2D cartesian domain**
  - 3D cartesian, 2D axisymetric domains --> realistic punctual leakage
- **Chemical processes**

  **Water phase speciation at equilibrium + mineral dissolution/precipitation**
  - --> addition of sorption processes

# Two leakage positions and inflow rates



# Intrusive fluid : two-phase and oxydative-acidic

- **The composition of the contaminant fluid is derived from a gas stream designed for injection in reservoir (Anheden et al., 2007) → contaminant fluid has maximal content of $SO_2$, NO and $O_2$ (1.5, 0.2 and 1.6 % respectively)**

  **→ strong hypothesis**

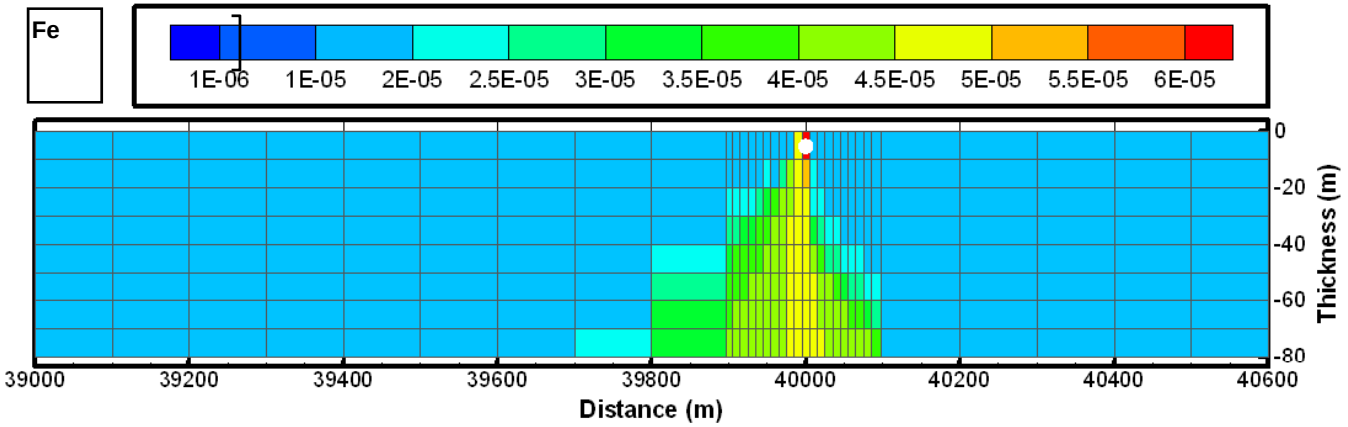
- **Intrusion of two-phase fluid (code limitation)**
  - Gaseous $CO_2$ + Water with impurities

  **→ Simulates the instantaneous dissolution-reaction of impurities in fresh water**

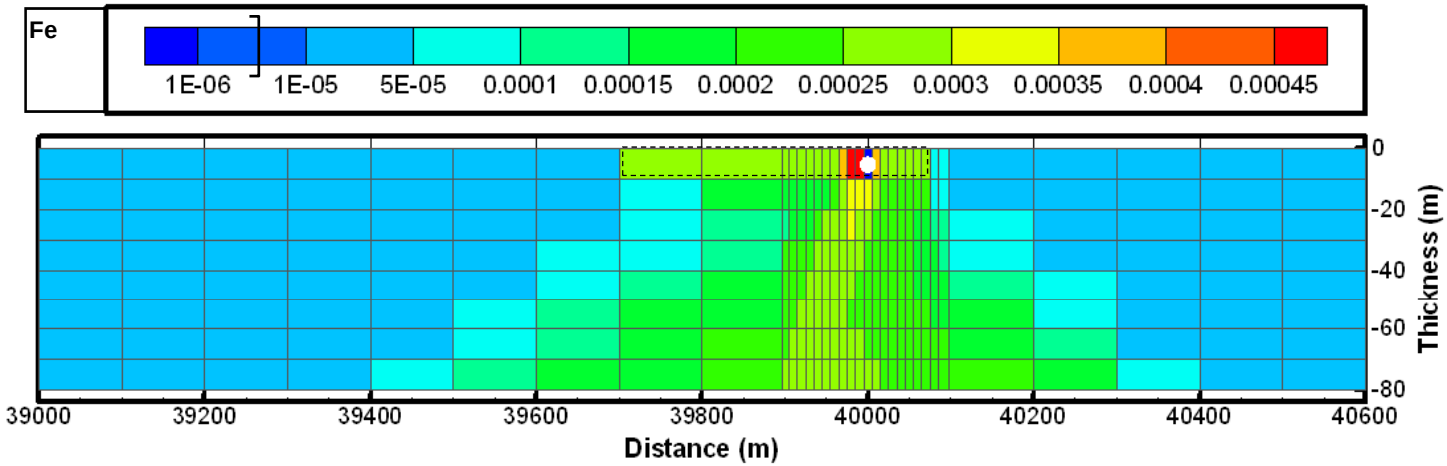
| | Fresh water | Water with impurities |
|---|---|---|
| **pH** | 7.4 | 0.4 |
| **pe** | -3,4 | 20.3 |
| **N** | - | 1.0e-01 |
| **N(+0)** | - | 5.0e-04 |
| **N(+5)** | - | 1.0e-01 |
| **S(+6)** | 3.5e-04 | 4.0e-01 |

- **Impurities-enriched water**
  - Result of oxyfuel gas stream dissolution
    - SO2 + 0.5 O2 + H2O → 2 H+ + SO42-
    - NO + 0.75 O2 + 0.5 H2O → H+ + NO3-
  - Oxydative and acidic
  - enriched in S(6) and nitrates N(5)
- **Systematic comparison with a pure CO2 intrusion to discriminate the SOx and NOx effect**

# Influence of flow rate : (1) concentrations amplitude and lateral extent



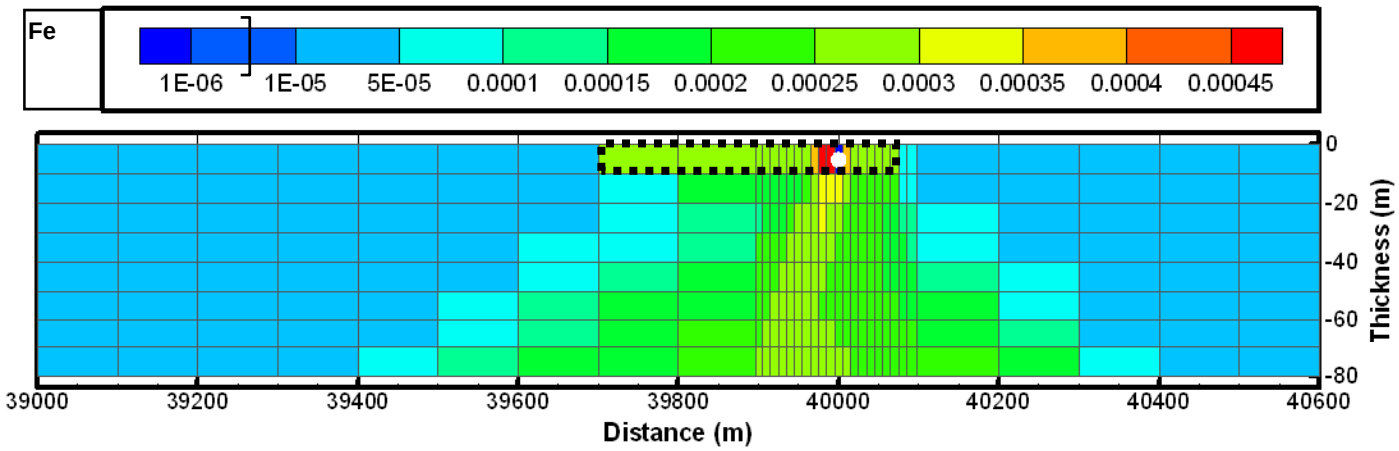

**Low rate**



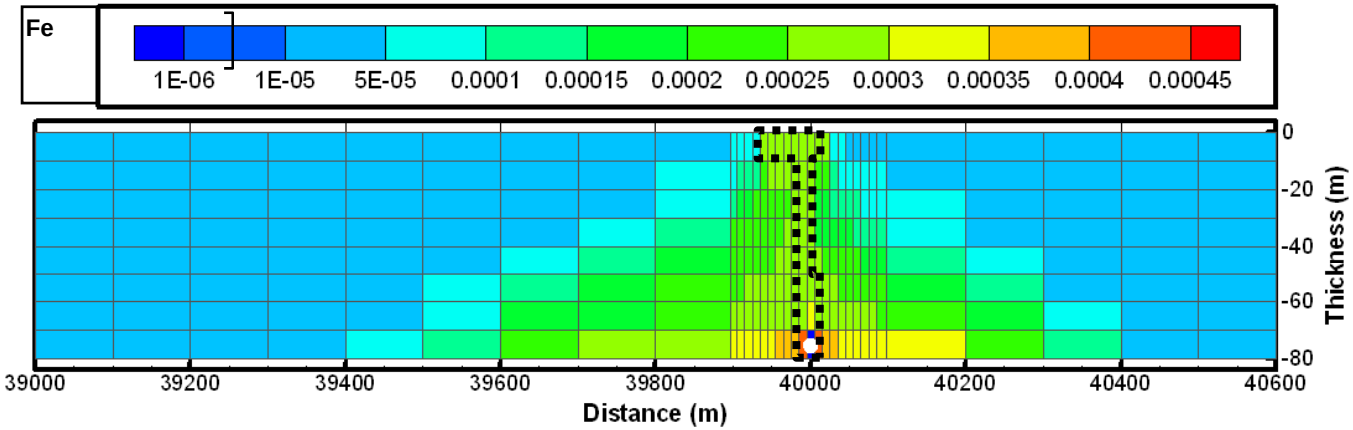

**High rate**

- **sdfg**

# Vertical extent due to gas plume upward migration



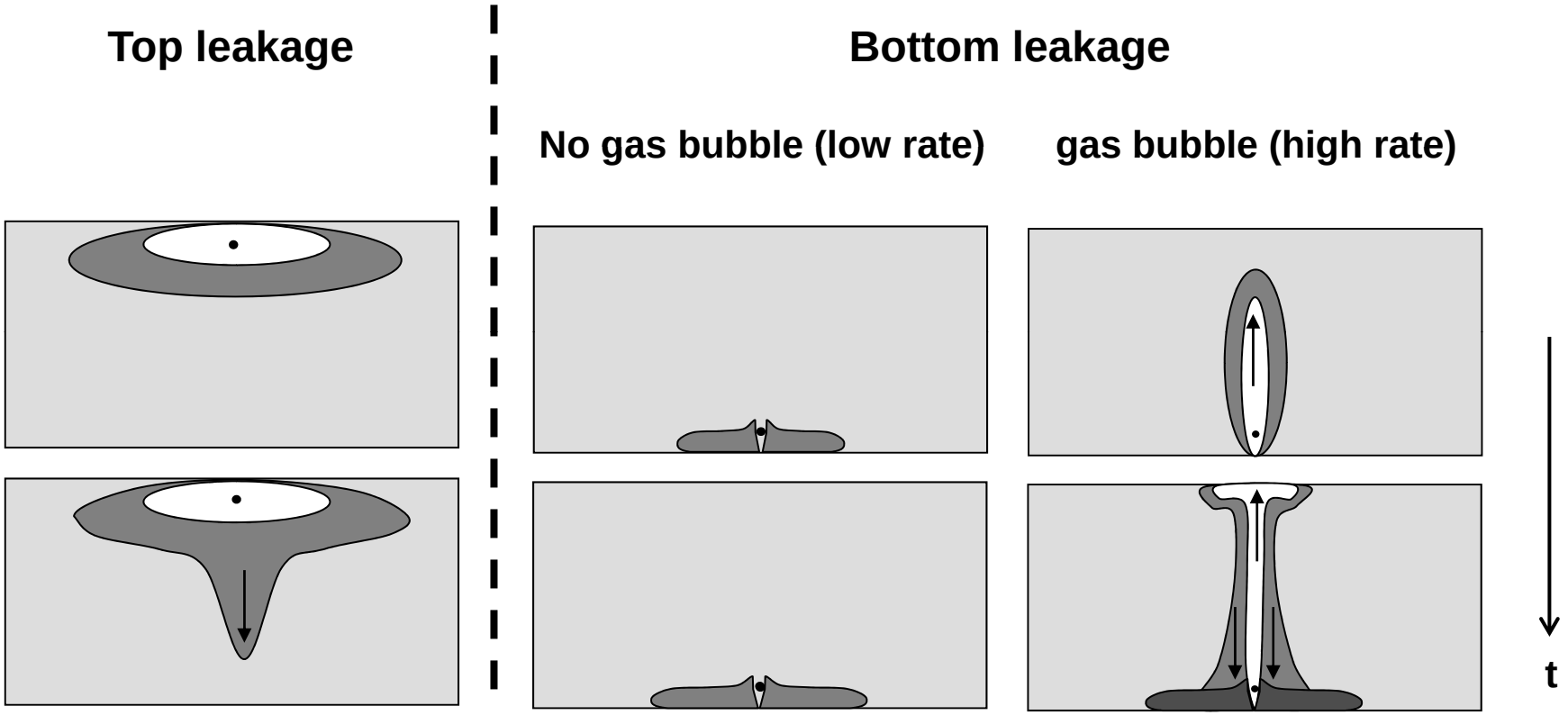

**Top leakage**




**Bottom leakage**

> **Flow rate sufficiently high to make appear a gas plume that migrates upward by gravity-contrast**

# Schematical spreading mechanims




> **+ groundwater regional flow**